

DYNAMIC EFFECTS IN GRADIENT THEORY FOR FLUID MIXTURES

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Abstract

We propose a new method to study motions of mixtures in fluid interfaces. We extend the equations of equilibrium in interfaces and the results associated with traveling waves for van der Waals like fluids [21]. Maxwell rule is extended to interfaces of fluid mixtures out of equilibrium. Formulae like Clapeyron relation are obtained for isothermal layers.

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1 Introduction

In this paper we propose a new attempt to study motions in interfaces of fluid mixtures. First, we recall the study of interfaces between mixture bulks in equilibrium. We remind problems for an interface moving in a single fluid and extend them to cases of mixtures.

How to calculate the proportions of constituents in each bulk of a n -components mixture? This problem is solved in the case of isothermal equilibrium for mixtures whose free energy is known [7]. A simple calculus consists in writing the total free energy of the mixture is minimum.

Practically, calculus are available only if:

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- the container has a simple shape allowing one dimension calculus (cylinder or sphere)
- the mixture has a few number of components
- the mixture free energy is not a too complex function of component densities and temperature.

Let us denote by ρ_i the density of constituent i ; $\rho = \sum_{i=1}^n \rho_i$ is the density of the mixture, $v = \frac{1}{\rho}$ the specific volume and $c_i = \frac{\rho_i}{\rho}$ the concentration of constituent i . The volume free energy at temperature θ is in the form $G_o = G_o(v, c_i, \theta)$. The total free energy is the sum of the thermodynamic free energy and the interfacial energy.

The determination of the function G_o is certainly of first importance, but it is not the topic of this paper. This is both a theoretical and an experimental problem and an equation of state with coefficients given by experiments is used for calculations. The free energy must be independent of the proportion of constituents when the density is vanishing [5,15,18].

In the case of flat interface, the knowledge of interfacial energy is not necessary for the calculation of balance equations between the bulks. The knowledge of interfacial energy is necessary to study spherical interfaces (bulks, drops, aerosols...). A Landau-Ginzburg model consisting in a quadratic form of density gradients representing the interfacial energy [12]. Coefficients of the quadratic form are assumed to be constant (in the case of a single fluid, this corresponds to a *mean field theory* [16]). A quadratic form of the gradients of specific volumes can be also used; nevertheless, assuming that the coefficients of the quadratic form are constant, it has a different physical meaning. In fact, the choice of a model is of no consequence outside of the interfacial layer. The Landau-Ginzburg model represents an interface and the bulks and builds a complete theory of the mixtures in dynamics [8,9,13].

In this paper, we apply the model to motions through interfaces for both single fluids and mixtures. Because of physic scales, motions can be often considered as permanent [4]. Interface moving in a single fluid was investigated by Slemrod [20-21] as a traveling wave whose image in a reference space is propagating with the constant velocity C . It is equivalent to say the fluid crosses a stationary interface with the flow q [4] (q is the product of velocity and density). When dissipative phenomena are neglected, the problem boils down to equilibrium with a specific free energy increased with $-\frac{1}{2} q^2 v^2$.

The general study of mixtures in dynamics can be applied in the case of

interfaces [9]. The constituent i crosses the interface with the flow q_i . We are back to a static problem with the same specific free energy and an additional term in the form

$$-\frac{1}{2} v^2 \sum_{i=1}^n \frac{q_i^2}{c_i}.$$

Each constituent of the mixture has its own reference space [1,9,17]. Due to the fact that the interface has different velocities in each reference space, the generalization of traveling wave is less intuitive.

For a n -component mixture, a permanent motion through an interface yields $n + 1$ equations of *dynamical* equilibrium. The equations represent a linear system of the $n + 1$ variables q_i^2 and θ . When the specific volume v and the concentrations c_i are given in each bulk, a simple calculus yields the temperature of the mixture and the flow for each constituent. Obviously, solutions are acceptable only if values q_i^2 and θ are positive.

Surprisingly, the problem of an interface in equilibrium is more difficult to study than the dynamical problem. It is more difficult to choose q_i^2 and θ (q_i is null in equilibrium case) and to deduce concentrations and specific volume than to choose concentrations and specific volume in each bulk and to deduce q_i^2 and θ from a system of linear equations.

2 Isothermal motion of a single fluid in the "Korteweg - van der Waals" theory of capillarity.

Let us consider the one dimensional motion of van der Waals like fluid. We notice that the same equations describe a traveling wave of dynamic phase transition and a flow through an interface in the case of permanent motion.

M. Slemrod [21] consider the one-dimensional motion of fluid possessing a specific free energy of the form¹:

$$G(v, \theta) = G_o(v, \theta) + \frac{e}{2} \left(\frac{\partial v}{\partial X} \right)^2$$

where X is the lagrangian mass variable, e is a small positive parameter. In the referential space, the balance laws of motion may be written in the form:

¹ The notations are different from the ones given in [20-21]

$$\begin{cases} \frac{\partial v}{\partial t} = \frac{\partial V}{\partial X} \\ \frac{\partial V}{\partial t} = \frac{\partial}{\partial X} \{-p(v, \theta) + \mu \frac{\partial V}{\partial X} - e^2 \frac{\partial^2 v}{\partial X^2}\} \\ \frac{\partial E}{\partial t} = \frac{\partial}{\partial X} \{v (-p + \mu \frac{\partial V}{\partial X} - e^2 \frac{\partial^2 v}{\partial X^2}) + e^2 (\frac{\partial V}{\partial X} \frac{\partial v}{\partial X}) + k \frac{\partial \theta}{\partial \xi}\} \end{cases} \quad (1)$$

where V denotes the velocity of the fluid, μ the viscosity, p the pressure, E the specific total energy, k the coefficient proportionality between the heat flux and the gradient of temperature in the Fourier Law and $\xi = X - Ct$. The traveling wave theory of phase transitions attempts to determine when two homogeneous phases may be joined by a traveling wave solution $\{v = v(X - Ct), V = V(X - Ct), q = q(X - Ct)\}$ of equations (1). Slemrod finds that the volume mass is solution of the equation:

$$e^2 \frac{d^2 v}{d\xi^2} = -C^2(v - v_o) - (p - p_o) - \mu C v \quad (2)$$

p_o and v_o denotes the values of p and v in the bulks. Because of the physical scales far from critical conditions, we established in [4] the motions of van der Waals fluids crossing interlayers can be considered as permanent. In the case of permanent motion of inviscid fluid, Eq. (1)₂ yields

$$\frac{dV}{dt} = \frac{d}{dx} \{-p(v, \theta) - e^2 \frac{\partial^2 v}{\partial X^2}\} v$$

where x denotes eulerian variable and $\frac{\partial x}{\partial X} = v$ [20]. From $V = q v$ where q denotes the constant flow of the fluid for an unidimensional permanent motion, we deduce:

$$e^2 \frac{\partial^2 v}{\partial X^2} = -q^2(v - v_o) - (p - p_o)$$

At t given, the form of the equation is similar to Eq. (2), which allows to obtain interpretations about dynamical Maxwell rule as in [20-21].

3 Isothermal motion of fluid mixture in the "Korteweg - van der Waals" theory of capillarity [9]

For the sake of simplicity, we study a mixture of two fluids. The method can be immediately extended to any number of constituents. No assumption has to be done about composition or miscibility.

The motion of a two-fluid continuum can be represented with two surjective differentiable mappings:

$$z \rightarrow X_1 = M_1(z) \quad \text{and} \quad z \rightarrow X_2 = M_2(z)$$

(Subscripts 1 and 2 are associated with each constituent of the mixture)

X_1 and X_2 denote the positions of each constituent in reference spaces D_{01} and D_{02} . The lagrangian of the mixture is:

$$L = \frac{1}{2} \rho_1 \mathbf{V}_1^2 + \frac{1}{2} \rho_2 \mathbf{V}_2^2 - \varepsilon - \rho_1 \Omega_1 - \rho_2 \Omega_2$$

where \mathbf{V}_1 and \mathbf{V}_2 denote the velocity vectors of each constituent, ρ_1 and ρ_2 are the densities, Ω_1 and Ω_2 are the extraneous force potentials depending only on $z = (t, x)$ and ε is the volume internal energy.

The expansion of the Lagrangian is in a general form. In fact dissipative phenomena imply that \mathbf{V}_1 is almost equal to \mathbf{V}_2 and we do not take into account some kinetic energy associated with the relative velocity of the components. Because of the interaction between the constituents, ε does not divide into energies related to each constituent of the mixture, like for *simple mixtures of fluids* [14]. The mixture is supposed to be no chemically reacting. Conservations of masses require:

$$\rho_i \det F_i = \rho_{oi} (X_i) \quad (3)$$

where subscript i belongs to $\{1, 2\}$. At t fixed, the Jacobian associated with M_i is denoted by F_i and ρ_{oi} is the reference specific mass in D_{oi} .

In differentiable cases, Eq. (3) is equivalent to:

$$\frac{\partial \rho_i}{\partial t} + \operatorname{div} \rho_i \mathbf{V}_i = 0$$

The volumic internal energy ε is given by the thermodynamic behavior of the mixture. Each constituent has a specific mass; in the same way, two specific entropies s_1 and s_2 are supposed to be associated with constituents 1 and 2.

For an internal energy depending on gradients of densities, the volume internal energy is:

$$\varepsilon = \varepsilon(s_1, s_2, \rho_1, \rho_2, \operatorname{grad} \rho_1, \operatorname{grad} \rho_2) \quad (4)$$

The quantity

$$h_i = \varepsilon_{,\rho_i} - \varepsilon_{,\rho_i,\gamma,\gamma}$$

defines the specific enthalpy of the constituent i of the mixture. Subscript γ corresponds to the spatial derivatives associated with gradient terms; as

usually, summation is made on repeated subscript γ .

$$\theta_i = \frac{\varepsilon_{,s_i}}{\rho_i}$$

defines the temperature of the constituent i of the mixture.

In practise we use the expression

$$\varepsilon = \alpha(s_1, s_2, \rho_1, \rho_2) + \frac{1}{2} Q$$

where Q is a quadratic form with constant coefficients:

$$Q = C_1 (\text{grad } \rho_1)^2 + 2D \text{grad } \rho_1 \text{grad } \rho_2 + C_2 (\text{grad } \rho_2)^2$$

and $\alpha(s_1, s_2, \rho_1, \rho_2)$ is the value of internal energy in the homogeneous bulks.

To obtain the equations of motions, we used variational principle whose original feature is to choice variations in reference spaces (Fig. 1) [9].

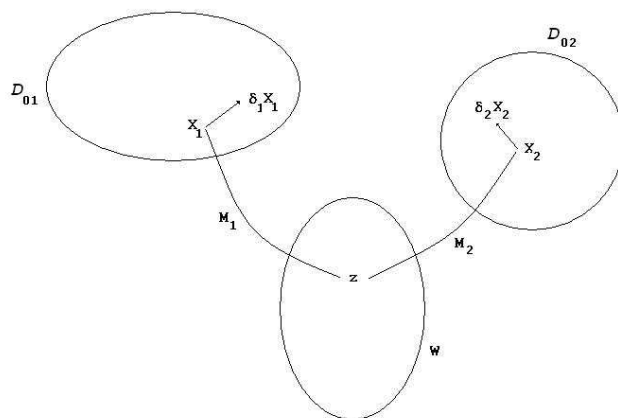


Figure 1

Variations δ_1 and δ_2 of motions of particles are deduced from $X_1 = \psi_1(x, t, \beta_1)$ and $X_2 = \psi_2(x, t, \beta_2)$. They are associated with a two-parameter family of virtual motions of the mixture. The real motion corresponds to $\beta_1 = 0$ and $\beta_2 = 0$.

Obviously, a classical variation of function in space W (as Serrin's p. 145, [19]) with only one parameter cannot give as many informations as the ones given by any two-parameters family of virtual displacements.

The equation of the motion of each constituent of the mixture is:

$$\Gamma_i = \theta_i \text{grad } s_i - \text{grad } (h_i + \Omega_i) \quad (5)$$

Let us note that the motion of each constituent is described by the same equation that for a single fluid [10,19]. In applications, the motions are supposed to be isothermal and $\theta_i = \theta$ (θ common temperature value for all the components). This case corresponds to strong heat exchange between components.

Eq. (5) yields:

$$\Gamma_i + \text{grad } (\varphi_i + \Omega_i) = 0$$

where $\varphi_i = h_i - \theta s_i$ is the free specific enthalpy (or chemical potential) of constituent i . In the bulks, the volumic free energy associated with α is denoted by $g_o = g_o(\rho_1, \rho_2, \theta)$. A complete study of the barycentric motion of the mixture and of the equation of energy is given in [9]. This generalizes results for single fluid [3,6,11].

4 Motion of an isothermal fluid mixture through a plane interface

An interface in a two-phase mixture is generally schematized by a surface without thickness. Far from critical conditions, this layer is of molecular size and density and entropy gradients are very large. A continuous model schematizes such areas by using an energy in form (4) extending forms given in [2,16] for compressible fluids.

For the same reasons than for a single fluid, motion is supposed to be isothermal, stationary and one dimensional with respect to x .

The acceleration of component i is:

$$\Gamma_i = \frac{1}{2} \frac{d}{dx} \left(\frac{q_i^2}{\rho_i^2} \right).$$

and the equations of motion yield:

$$\begin{cases} \Gamma_1 = \text{grad } \{C_1 \Delta \rho_1 + D \Delta \rho_2 - g_{o, \rho_1}\} \\ \Gamma_2 = \text{grad } \{D \Delta \rho_1 + C_2 \Delta \rho_2 - g_{o, \rho_2}\} \end{cases}$$

or:

$$\begin{cases} C_1 \rho_1'' + D \rho_2'' = g_{o,\rho_1} + \frac{1}{2} \frac{q_1^2}{\rho_1^2} + k_1 \\ D \rho_1'' + C_2 \rho_2'' = g_{o,\rho_2} + \frac{1}{2} \frac{q_2^2}{\rho_2^2} + k_2 \end{cases}$$

(The derivatives along the motion axis are denoted by ').

Combination of the last two equations yields the first integral:

$$g_o + k_1 \rho_1 + k_2 \rho_2 - \frac{1}{2} \frac{q_1^2}{\rho_1} - \frac{1}{2} \frac{q_2^2}{\rho_2} - \left(\frac{1}{2} C_1 \rho_1'^2 + D \rho_1' \rho_2' + \frac{1}{2} C_2 \rho_2'^2 \right) = k_3$$

In each bulk, densities have zero-gradients. Eliminating constants k_i , dynamical conditions through the interfacial layer yield:

$$\begin{cases} [g_{,\rho_1}(\rho_1, \rho_2)] = 0 \\ [g_{,\rho_2}(\rho_1, \rho_2)] = 0 \\ [g - \rho_1 g_{,\rho_1} - \rho_2 g_{,\rho_2}] = 0 \end{cases} \quad (6)$$

where [] denotes the discontinuities through the layer and

$$g = g_o - \frac{1}{2} \frac{q_1^2}{\rho_1} - \frac{1}{2} \frac{q_2^2}{\rho_2}.$$

In case of equilibrium (q_1 and q_2 are null), the minimum of the total free energy, with a given total mass for each constituent, yields conditions (6).

By adding the term $-\frac{1}{2} \frac{q_1^2}{\rho_1} - \frac{1}{2} \frac{q_2^2}{\rho_2}$ to g_o , the study of flat interfaces crossed by components of a mixture turns back to an equilibrium problem. In fact, a complete study of the thickness of the interfacial layer or of spherical interfaces of microscopic size requires the non-linear model.

It is more classical to use the variables v or c . The mapping $(\rho_1, \rho_2, g) \rightarrow (v, c, G)$ where $v = \frac{1}{\rho_1 + \rho_2}$, $c = \frac{\rho_2}{\rho}$, $G_o = \frac{g_o}{\rho}$ and $G = G_o - \frac{1}{2} v^2 \left(\frac{q_1^2}{1-c} + \frac{q_2^2}{c} \right)$, allows to write

$$\begin{cases} [G_{,v}(v, c)] = 0 \\ [G_{,c}(v, c)] = 0 \\ [G - v G_{,v} - c G_{,c}] = 0 \end{cases} \quad (7)$$

Conditions (6) or (7) express that the points corresponding to the bulks of the Gibbs surface (Σ) associated with the dynamical free energy g or G are

contact points of a bitangent plane (Fig. 2).

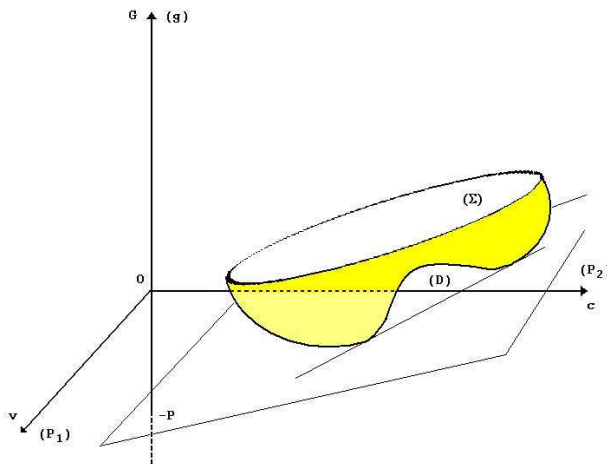


Figure 2

The pressure of the mixture is $p = -G_{o,v}(v, c)$, the dynamical pressure is $P = -G_v(v, c)$.

The z -coordinate of the point of intersection of the bitangent plane with the g -axis is $-P$. The chemical potential G_c is denoted by Φ .

Contact points of the bitangent plane with surface (Σ) generate a curve. Along this curve, the straight line (D) connecting the contact points is the *characteristic line* of the plane. Along the line, the relation

$$(v - v_0) dG_v + (c - c_0) dG_c = 0$$

allows to generalize Clapeyron formula such that:

$$\frac{dP}{d\Phi} = \frac{c_1 - c_0}{v_1 - v_0}$$

where subscripts 0 and 1 are associated with the two bulks.

5 Maxwell rules for fluid mixtures

At a given temperature θ , the differential form $dG = -P dv + \Phi dc$ yields the relation:

$$\int_{(C)} (\Phi - \Phi_0) dc - (P - P_0) dv = 0$$

where (C) is an arbitrary curve connecting the two bulks in the space (c, v) . The common values of Φ and P in the bulks are denoted by Φ_0 and P_0 .

We can calculate the integral along special paths:

Along the curve (C) given by the implicit function $c(v)$ defined such that $G_{,c}(c(v), v) = \Phi_0$, the relation

$$\int_{(C)} (P - P_0) dv = 0$$

represents the Mawxell equal area rule for the path $\overline{\mathbf{abcd}}$ in the plan (P, v) where² $P = -G_{,v}(c(v), v)$

Likely, for $P = P_0$, the relation:

$$\int_{(C)} (\Phi - \Phi_0) dc = 0$$

represents the Mawxell equal area rule for the path $\overline{\mathbf{abcd}}$ in the plan (c, Φ) where $\Phi = G_{,c}(c, v(c))$ is such that v is expressed as a function of c by the relation $G_{,v}(c, v(c)) = -P_0$.

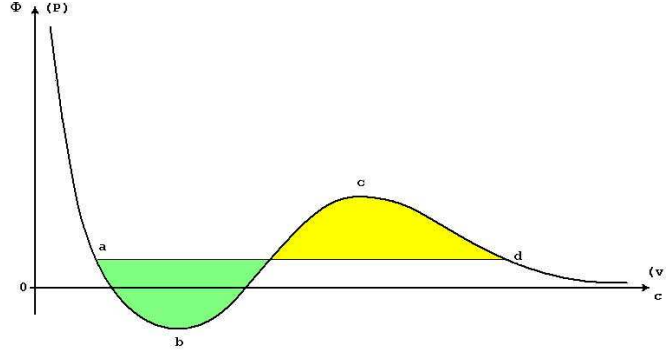


Figure 3

These results generalize the ones obtained by Slemrod in the case of inviscid flows of single fluids [21]. The knowledge of the free specific energy G_o is sufficient to solve the previous problem. Function G_o is obtained by integration of the equation of state $p = p(v, c, \theta)$:

$$\frac{\partial G_o(v, c, \theta)}{\partial v} = -p(v, c, \theta) \quad (8)$$

Function p is determined except for an additional function of c and θ . With the physical assumption that G_o is independent of c when v vanishes, the additional function depends only on θ .

² (C) is not the curve associated with $P = P(c, v)$ at c constant.

The simplest model of equation of state is by van der Waals:

$$p = \frac{R\theta}{v-b} - \frac{a}{v^2} \quad (9)$$

where a and b are given by the mixing rules:

$$a^2 = (1-c)a_1^2 + ca_2^2 \quad \text{et} \quad b = (1-c)b_1 + cb_2 \quad (10)$$

(Subscripts 1 and 2 are associated with the components 1 and 2).

One deduces: $G_o = -R\theta \ln(v-b) - \frac{a}{v}$.

Other equations of state are proposed for example $p = \frac{R\theta}{v-b} - \frac{a}{v(v+b)}$ (particularly in petroleum industry [5,15,18]) or by changing the form of the mixing rules (other expressions than $a^2 = \sum_{i=1}^n a_i^2 c_i$ and $b = \sum_{i=1}^n b_i c_i$ can be considered).

Equations (7), (8), (9) and (10) lead to the system:

$$\begin{cases} \left[\frac{\theta}{v-b} + \frac{v}{1-c} q_1^2 + \frac{v}{c} q_2^2 - \frac{(b+1)^2}{v^2} \right] = 0 \\ \left[\theta \left\{ 1 - \ln(v-b) + \frac{b_1}{v-b} \right\} + \frac{1}{2} \frac{v^2}{(1-c)^2} q_1^2 - 2 \frac{(b_1+1)(b+1)}{v} \right] = 0 \\ \left[\theta \left\{ 1 - \ln(v-b) + \frac{b_2}{v-b} \right\} + \frac{1}{2} \frac{v^2}{c^2} q_2^2 - 2 \frac{(b_2+1)(b+1)}{v} \right] = 0 \end{cases}$$

which is a linear system with respect to θ, q_1^2, q_2^2 .

6 Conclusion

The study of fluid mixture motions by a model taking into account density gradients of components requires the knowledge of the global free energy. In fact, only physical experiments and molecular theories provide an equation of state (in van der Waals type). Isothermal motions can be studied by using such an equation and yield the jump conditions through interfacial layers. To carry the program one step further and to study non-isothermal motions, it is necessary to get additional knowledges (such that specific heats...).

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